

Diamond Like Carbon Coating Produced by Plasma Source Ion Implantation as a Corrosion Barrier for Steels in Marine Environments

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Abstract

A36 steel samples coated with diamond like carbon (DLC) produced by plasma source ion implantation (PSII) were examined in ASTM artificial ocean water (ASTM AOW). To evaluate the coating's susceptibility to breakdown in a marine environment, electrochemical impedance spectroscopy experiments were conducted on coated samples immersed in ASTM AOW for a 2 month period. Results determined that while the coating was susceptible to corrosion at pre-existing defects, however, breakdown was not catastrophic for the first 20 days of immersion. In comparison, earlier work on DLC coated Ni samples with fewer defects per unit area found that the Ni/DLC system failed catastrophically via pitting corrosion within 24 hrs. In contrast the DLC coated steel samples examined here appeared to suffer from a more generalized corrosion at the pre-existing defects. Potentiodynamic polarization experiments on "as received" A36 steel samples confirmed that the steel was susceptible to pitting attack in this environment and experiments on carbon implanted samples (the surface preparation used in PSII) were susceptible to preferential dissolution of iron from the matrix. Both of these observations were also found in the examination of DLC coated Ni samples. Here, however, the build up of iron corrosion product at pre-existing defects was observed. It appears that the build up of this product was sufficient to mitigate propagation of pitting attack. These results indicate that DLC may provide adequate corrosion protection if the concentration of defects per unit area can be decreased.

Introduction

There currently exists a broad range of applications for which the ability to produce an adherent, hard, wear, and corrosion-resistant coating plays a vital role. These applications include engine components, orthopedic devices, textile manufacturing components, hard disk media, optical coatings, and cutting and machining tools (e.g., punches, taps, scoring dies, and extrusion dies). Plasma-based ion beam processing can play an important role in all of these technologies. The ability to provide flux, energy, and temporal control of a variety of ions, provides an avenue to tailor surface structure and chemistry necessary to solve current and future problems related to corrosion, surface hardness and tribological properties. Ion implantation is a well established ion beam based surface modification technique which has been successfully used to enhance materials engineering performance in areas such as, hardness[1], friction and wear[2], fracture toughness, and corrosion [3,4,5,6].

Plasma source ion implantation (PSII), has the potential to overcome the limitations of conventional ion implantation by: (1) reducing the time and expense for implanting complex shapes and large areas, and (2) extending the thickness of the modification zone through ion beam enhanced plasma growth of surface coatings. In PSII, targets are placed directly in a plasma source and then pulse biased to produce a non-line-of-sight process for complex-shaped targets without complex fixturing. If the pulse bias is a relatively high negative potential (20 to 100 kV) ion implantation will result. If however, a low voltage (50 - 1200 eV) high duty cycle pulse bias is applied, film deposition from the chamber gas will result, thereby increasing the extent of the surface modification into the 1–10 micron regime.

Experimental

Navy designation A36 steel rod stock (5/8" diam) was cut into disks approximately 1/4" thick. These samples were polished to a 0.30 μm finish. The samples were then degreased and ultrasonically cleaned, after which they were placed in an ion implantation chamber where the

native oxide was removed by sputter etching with argon (Ar) for one hour. This sputter cleaning was immediately followed by carbon (C) implantation from methane at 30 kV. Carbon implantation prior to coating with DLC improves the adhesion properties of the DLC. After implantation, the surface was sputter cleaned for approximately 15 minutes. DLC was then deposited onto this surface from an RF plasma of acetylene (4.5 mTorr total pressure). The final DLC thickness was approximately 4-5 microns[7]. Transmission electron microscopy of similar specimens have shown the DLC structure to be amorphous[8]. The DLC coating had a density of 1.9 g/cm³ and consisted of approximately 70 at% C and 30 at% hydrogen (H). The C:H ratio was found to greatly effect coating properties with lower hydrogen content yielding coatings with the highest hardness values.

To simulate a marine environment, corrosion experiments were conducted in ASTM Artificial Ocean Water[9]. The constituents are presented in Table 1. Because this solution contained a high concentration of chloride, a Saturated Calomel Electrode (SCE; +0.241 vs. Normal Hydrogen Electrode) was used as a reference.

Table 1 Constituents in ASTM Artificial Ocean Water [9].

constituent	concentration g/L
NaCl	24.53
MgCl₂ ♦ 6H₂O	5.20
Na₂SO₄	4.09
CaCl₂ ♦ 2H₂O	2.2
KCl	0.695
NaHCO₃	0.201
KBr	0/101
H₃BO₃	0.027
SrCl₂ ♦ 2H₂O	0.025
NaF	0.0003

EIS experiments were conducted at the Open Circuit Potential (OCP) over the frequency range of 1×10^{-2} - 4.0×10^4 Hz. Data were collected in this frequency range at 10 points per decade of frequency. Prior to EIS measurements the OCP was monitored for 1 hour to insure steady state. Anodic and cathodic polarization curves were generated at a sweep rate of 0.1 mV/sec after 1.5 hours at the OCP to insure steady state.

Results

DLC Coated A-36 in ASTM AOW An optical micrograph of the DLC coated steel surface prior to exposure to the test solution is presented in Figure 1. As shown in this micrograph numerous defects 0.04 mm and smaller were observed in the DLC coating.

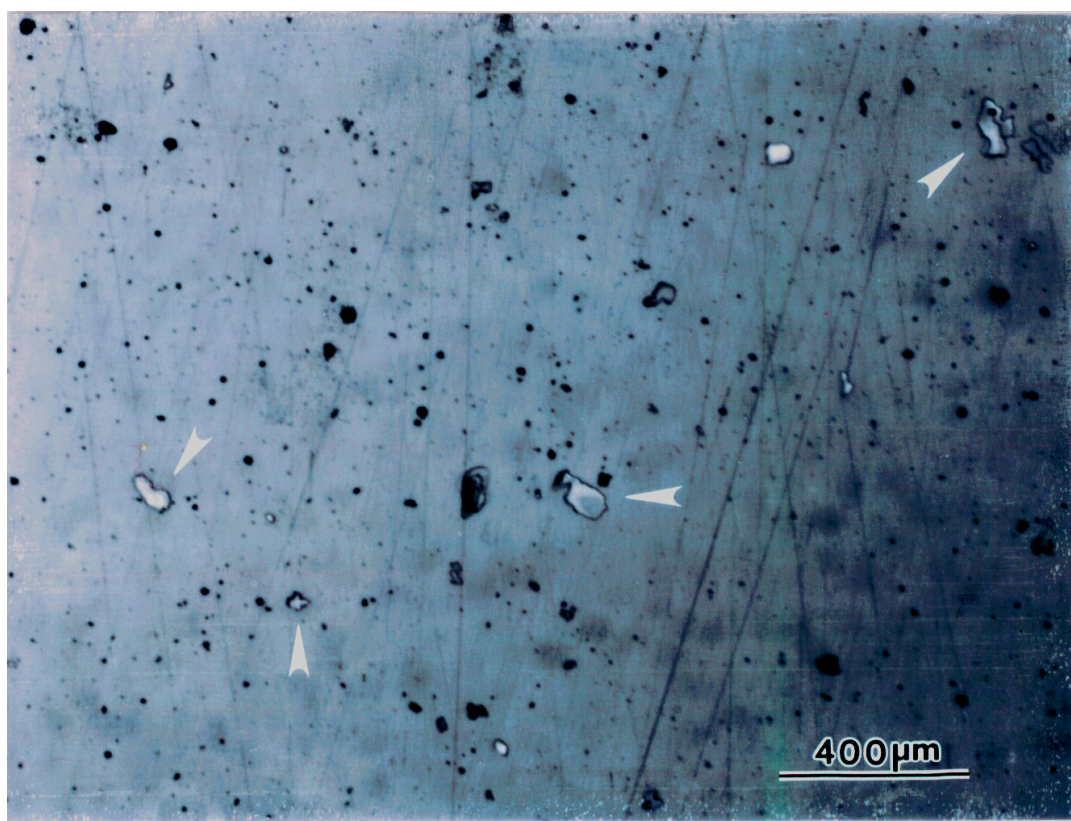


Figure 1 Optical micrograph of DLC surface prior to immersion in ASTM AOW. Arrows denote defects in the coating formed during the deposition process

Two DLC coated steel samples were immersed in ASTM artificial AOW for a 2 month period. Representative Bode magnitude and phase plots for one sample are shown in Figure 2a and 2b for immersion times of 1 hr, 1, 20, and 63 days. It has been demonstrated that these data may be modeled as the equivalent circuit shown in Figure 3[10]. In our system the intrinsic electrical properties of the carbon implanted layer are represented by the elements C_{IL}^i and R_{IL}^i , where the superscript 'i' represents "intrinsic". This layer acts in series with the DLC coating represented by the elements C_{DLC}^i and R_{DLC}^i which model the capacitance and charge transfer resistance of the DLC. The elements representing the carbon implanted layer and DLC act in parallel with small "pinholes" in the DLC (Figure 1). These pinholes expose either the carbon implanted layer, a very thin DLC layer, or a combination of both. As will be shown later in this paper, these pinholes act as initiation sites for breakdown and are, therefore, associated with a double layer capacitance and corrosion resistance, C_{dl}^i and R_{corr}^i respectively. The fraction of surface covered by these pinholes is defined by Θ and the fraction of surface covered by DLC is defined by $1-\Theta$. The observed (measured with EIS) parameters will necessarily scale with Θ . These 'observed' elements are represented by a superscript 'o'. For example: $R_{corr}^o = R_{corr}^i/\Theta$ and $R_{DLC}^o = R_{DLC}^i/(1-\Theta)$.

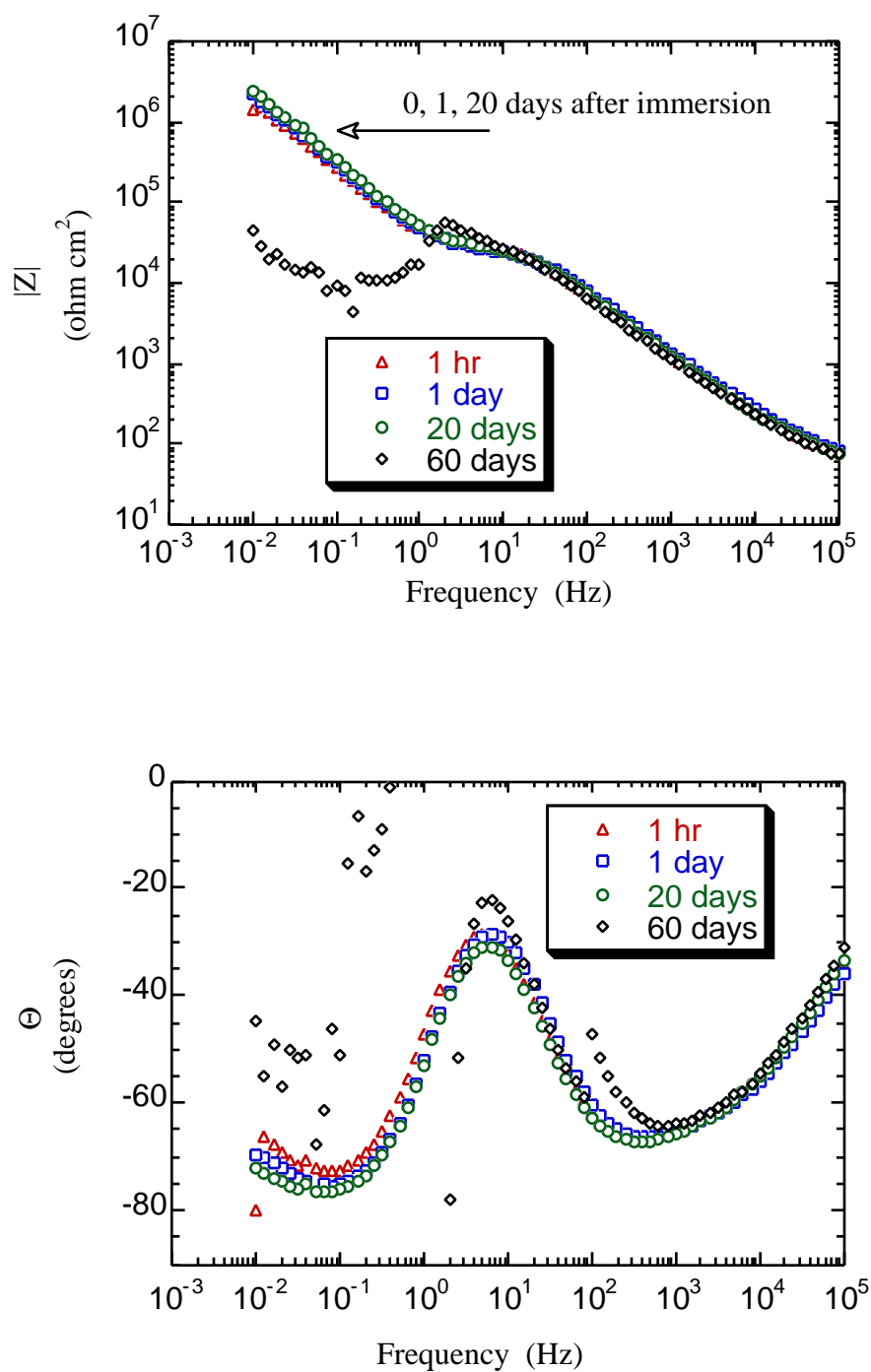


Figure 2 Bode Magnitude (a) and Bode phase (b) plots for DLC coated A-36 steel in ASTM artificial ocean water. Data collected at the samples OCP (rest potential).

The Bode magnitude data in Figure 2a indicates no growth of the pin-holes or change in the polarization resistance after 20 days of immersion in the test solution. Had such changes occurred, a drop in the intermediate (1-10 Hz) and low frequency (less than 0.1 Hz) impedances would have been observed. After 60 days of immersion in ASTM artificial ocean water, significant changes in both the intermediate (1-10 Hz) and low frequency (less than 0.1 Hz) impedances were observed. These changes indicate catastrophic failure of the coating and corrosion of the underlying A-36 steel. Similar results were obtained for a duplicate sample with only slightly different surface preparations.

Upon removal from the test solution after the 60 day immersion period, large (greater than 0.2 mm) corrosion defects were observed in the DLC coating (Figure 4). At the base of these defects copious amounts of iron corrosion product was observed. In addition, the DLC coating appeared to be shiny, as if slightly electrochemically "polished" during the immersion period.

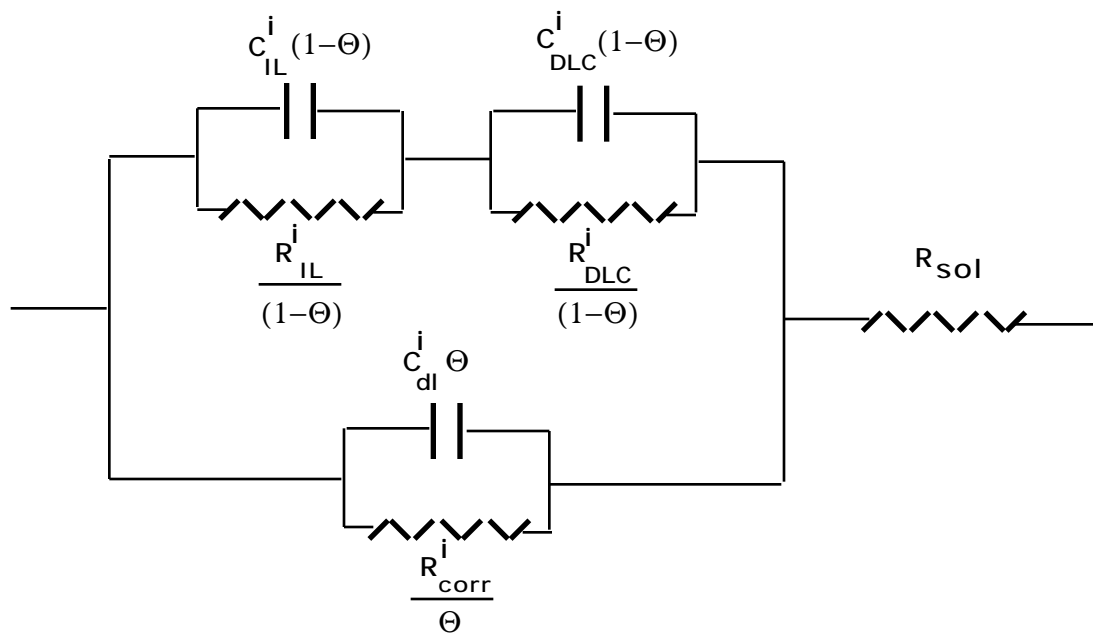
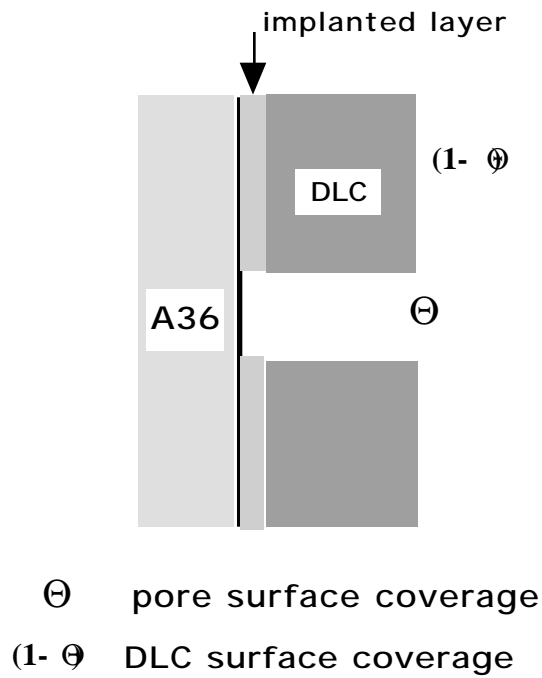


Figure 3 a) Schematic diagram representing the layers in DLC coating and a defect native to the coating b) electrical equivalent circuit model representing the breakdown of DLC coated A-36 steel in NaCl solution.

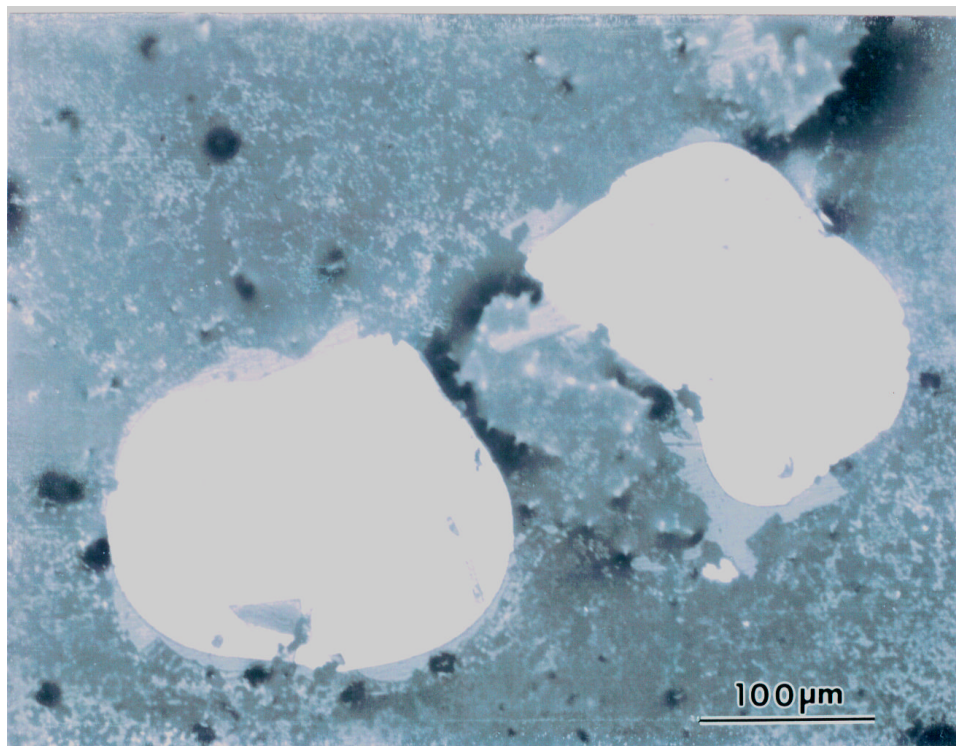
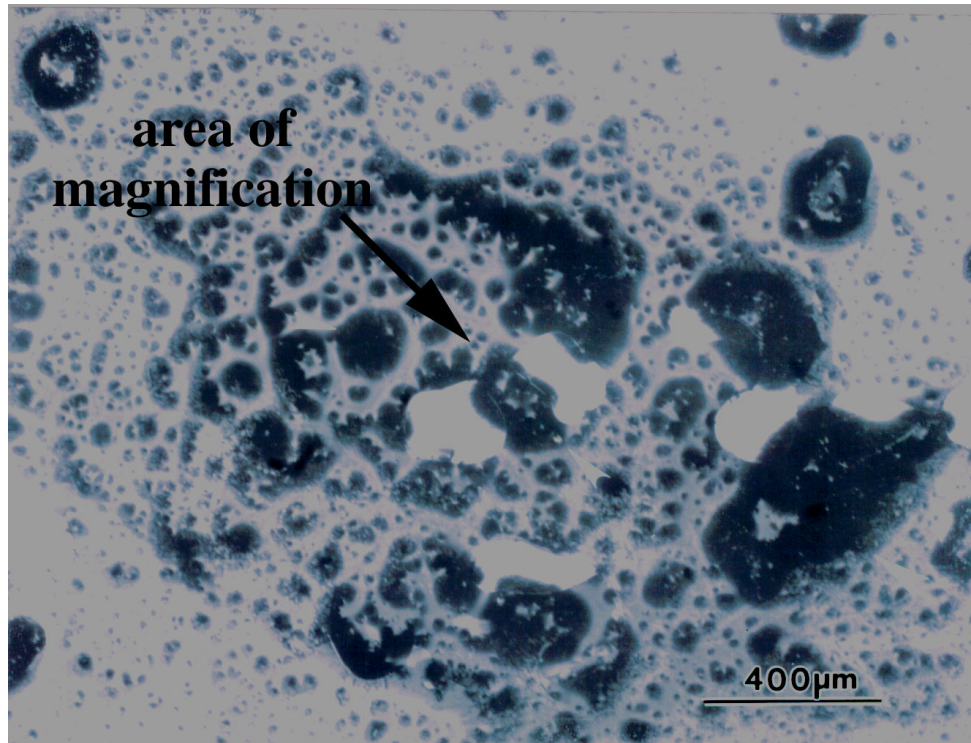


Figure 4 Optical micrographs of DLC coated A36 steel after 2 months of immersion in ASTM artificial ocean water (**b** is a magnification of area in **a** as noted).

A-36 Steel in ASTM AOW Potentiodynamic polarization curves for as polished A-36 steel and carbon implanted A-36 steel in ASTM artificial ocean (ambient aeration) are presented in Figure 5. Between its OCP and approximately +0.15 V SCE, as polished A-36 is passive in ASTM AOW. As represented by the sharp increase in current at approximately +0.16 V SCE (E_{pit}), as polished A-36 steel is susceptible to pitting type attack in this solution. While the carbon implanted A-36 also pits at approximately +0.16 V SCE, the carbon raises the OCP of this material sufficiently such that the OCP is equal to E_{pit} . While the DLC coating may provide some protection from breakdown in marine environment, these data indicate that the carbon implanted layer increases the susceptibility of the steel to pitting attack possibly due to a local galvanic effect.

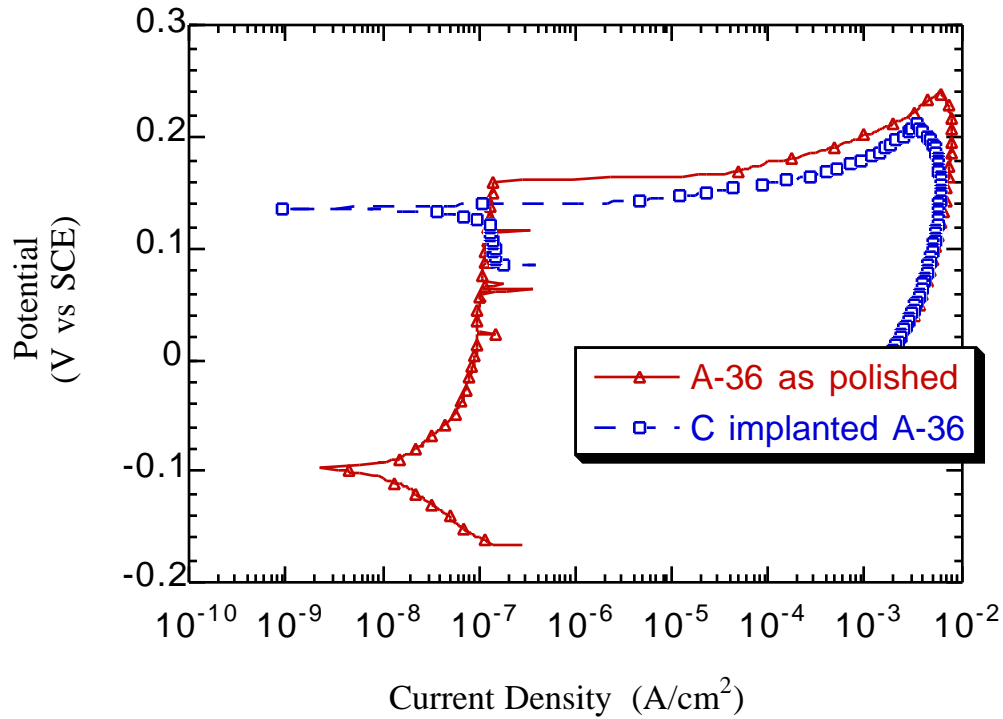


Figure 5 Potentiodynamic polarization curves for as polished A-36 and carbon implanted A-36 in ASTM artificial ocean water (ambient aeration).

Conclusions

A36 steel samples coated with diamond like carbon (DLC) produced by plasma source ion implantation (PSII) were examined in ASTM artificial ocean water (ASTM AOW). This solution was chosen to simulate a marine environment. To evaluate the coating's susceptibility to breakdown, electrochemical impedance spectroscopy experiments on coated samples immersed in ASTM AOW for a 2 month period. Results determined that while the coating was susceptible to corrosion at pre-existing defects, breakdown was not catastrophic for the first 20 days of immersion. Possible methods for mitigating breakdown include:

- Optimization of DLC deposition parameters to minimize defects
- Sputter coating / ion implanting A-36 surface with Cr or Mo prior to coating with DLC
- Using PSII to implant N into the A-36 surface prior to coating with DLC

References

- 1 J. Robertson, **Progress in Solid State Chemistry**, vol. 21, no. 1, pp. 199- , 1991
- 2 K.C. Walter, M. Nastasi, H. Kung, P.Kodali, C. Munson, I. Henins, B.P. Wood, "Diamond-Like Carbon Deposition for Tribological Applications at Los Alamos National Laboratory", in *Materials Research Society Symposium Proceedings*, Volume 383, MRS, Pittsburgh, pp 411-22, 1995.
- 3 A.H. Al-Saffar, V. Ashworth, A.K.O. Bairamov, D.J. Chivers, W.A. Grant, R.P.M. Procter, **Corrosion Science**, vol. 20, no. 1, pp. 127-34, 1980.
- 4 Ashworth,V.,R.P.M. Procter, and W.A. Grant,"The Application of Ion Implantation to Aqueous Corrosion" in Ion Implantation, ed. J.K. Hirvonen, Academic Press (1980), New York.
- 5 P.M. Natishan, E. McCafferty, G.K. Hubler, **The Journal of the Electrochemical Society**, vol. 135, no. 2, pp. 321-327, 1987.
- 6 C.R. Clayton, in Passivity of Metals and Semiconductors, eds.M. Froment, Elsevier(1983), Amsterdam, pg.305.
- 7 D.P. Butt, K.C. Walter, M. Nastasi, A.L. Campuzano, P.S. Martin, B.P. Wood, D.J. Rej, G.G. Miller, **Philosophical Magazine Letters**, vol. 70, no. 6, pp. 385-87, 1994.
- 8 M. Nastasi, J.P. Hivonen, G.M. Pharr, W.C. Oliver, **Journal of Materials Research**, vol. 3, no. 2, pp. 226-32, 1988.
- 9 ASTM D1141, Annual Book of Standards, ASTM, Philadelphia, 1987.
- 10 R.S. Lillard, D.P. Butt, T.N. Taylor, K.C. Walter, M. Nastasi, "The Breakdown Mechanism of Diamond Like Carbon Coated Nickel in Chloride Solutions", accepted for publication in **Corrosion Science**, September, 1996